# This Page Is Inserted by IFW Operations and is not a part of the Official Record

# **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

# IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

#### (9) 日本国特許庁 (JP)

⑪特許出願公開

# ⑫ 公 開 特 許 公 報 (A)

昭58—109179

50Int. Cl.3 C 02 F 1/22 識別記号

庁内整理番号 6685---4 D

砂公開 昭和58年(1983)6月29日 発明の数 1

審查請求 未請求

(全 4 頁)

#### **匈LNG直接々触冷凍海水淡水化方法**

昭56-206983 ②特

昭56(1981)12月23日 ②出

渕上武彦 ⑫発 明 者

座間市相模が丘2丁目39番25号

明 二階堂信夫 79発 者

東京都太田区田園調布 4 丁目20

番13号

西村成興 明 ⑫発 者

日立市幸町3丁目1番1号株式

会社日立製作所日立研究所内

70発 明 者 安達哲朗

会社日立製作所日立研究所内 六t串俊巳 明

79発

日]立市幸町3丁目1番1号株式 会社日立製作所日立研究所内

日1立市幸町3丁目1番1号株式

江厂原勝也 明 79発 者

> 日1立市幸町3丁目1番1号株式 会长社日立製作所日立研究所内

東夏京瓦斯株式会社 创出 願

東夏京都中央区八重州1丁目2番1

6号

弁4理士 高橋明夫 個代 理 人

最終頁に続く

#### 岄

発明の名称 LNG直接々触冷凍海水淡水化方 佉

#### 特許請求の範囲

1. LNGをガス化するLNG気化方法において、 LNGと海水とを直接々触させ、この直接々触に よつて生成したハイドレートを滅圧分解して氷に 変換せしめ、しかる後海水からこの氷を分離する と共に融解して淡水化することを特徴とする LNC直接々融冷凍海水淡水化方法。

2.ハイドレートの蔵圧分解時間を7分以上とし たことを特徴とする特許謂求の範囲第1項記載の LNG直接々触冷凍海水炎水化方法。

3. 氷の融解に使用した海水をLNGとの直接々 触に使用することを特徴とする特許請求の範囲第 1 項記載のLNG直接々触冷凍海水淡水化方法。 発明の詳細な説明

本発明はLNG(液化天然ガス)と海水とを直 桜々触させる海水淡水化方法に関する。

近年石油事情の悪化及びクリーンエネルギーへ

の指向からLNGの使用量が年々増加して来てい

LNGは産地にてて一160℃に冷却液化され、 消費地に輸送されるる。消費地では、加熱しガス化 して使用する。LNNGは冷熱として約200KcaL/ laを有するため、マイその有効利用を凶ることが消エ ネルギーの見地から重要視されている。

LNGのガス化7方式は従来より(1)オーブンラツ ク式、(2)サブマー:ジ式が採用されで来たが、両方 式ともLNGの持ごつている冷熱を有効利用するこ とができない。LINGの冷熱を利用する方法とし ては冷熱発電、低は温倉庫、海水炭水化などが考え られる。海水淡水f化を行なり方法としてはLNG の冷熱を高沸点の∂冷媒に移行させ、この冷媒と海 水を直接々触させ、る方法とLNGと梅水とを直接 接触させる方法で、ある。LNGと海水を直接々熈 させる方法は、熱も交換器がなく、その熱交換特性 は彼めて良好とな:り、LNGの冷熱を海水にりつ し、LNGをNGI(天然ガス)とすることができ る。この直接々触ま法のフローを第1図に示す。1

# 持開昭58-109179(2)

は梅水、2は梅水ポンプ、4はLNG、5はLNG ポンプであり、海水1とLNG4は晶析槽8内に おいて直接々触し、LNG4は海水に冷熱を移し NO3となるものである。この時、LNO4に対 する海水1の量を削減して行くことにより、海水 中に氷晶とハイドレート(炭化水素の水和物)が 生成する。ハイドレードの生成量はLNGの組成、 晶析圧力、晶析温度により変化する。 なお 6 はプ ラインポンプ、7はプラインである。第2図は CH, 89 mol%のLNGのハイドレートの生成 域を示したもので、圧力10Kg/cm² G以上にな ると、その生成が顕著になつてくる。基礎検討の **結果ハイドレードが生成する領域ではハイドレー** トが氷よりも優先的に生成することが明らかにた つている。又、晶析圧力が10kg/cm2 G以下で はハイドレートはほとんど生成せず、氷の生成が **愛先的であることがわかつた。ハイドレートは第** 3 図(a)(b) に模式的に示したように、炭化水素分子 がその周囲を水分子の水素結合によりつつまれて いるもので、減圧により容易に中心の炭化水素が

阪圧分解して氷に変喫する分解槽、18は海水と 氷からなるスラリーを氷とプラインに分離する分 離僧、23は氷を海水26と間接々触させて融解 する融解槽である。19は分離槽18で分離され たプライン、20はそのプラインポンプ、21は プライン19の一部を晶析機13に循環する循環 水、22はその循環水ポンプ、24は融解槽23 で生成した淡水であり、その一部は分離槽18の 氷を洗浄するための洗浄水24Aとして用いられ る。25は 級解槽23で生成した 族水24 Bを分 離櫃18に循環させる循環ポンプ、27は淡水ポ ンプ、28は冷海水、29は洗浄水ポンプである。 さて、海水11は海水ポンプ12により晶析槽 13に送り込まれ、LNGポンプ14により供給 されたLNG15と直接々触する。LNG15は 海水11の熱を奪い、NG16となり、晶析槽 13から排出されるが、NGの一部は海水11と 反応してハイドレートが生成する。梅水とハイド レートからなるスラリーは、晶析槽13から分解 僧17へと移送される。分解槽17でハイドレー

ガス化し氷晶へと転ぶ換する。ハイドレートは結晶体であるが、LNG と海水との直接々触により生成したハイドレート1粒子の大きさは約40 μm程度であるので、固液2分離操作が困難でありハイドレートの状態での分r離洗浄法は実現性がない。

本発明は上記事情 (に鑑みなされたもので、LNG と海水とを直接々触して生成するハイドレートを 有効に淡水として回4収することを目的とするもの である。

即ち本発明の特徴をは、LNGをガス化するLNG 気化方法において、JLNGと海水とを直接々触させ、この直接々触に、よつて生成したハイドレート を滅圧分解して氷に3変換せしめ、しかる後海水からこの氷を分離する、と共に融解して。使水化する LNG直接々触冷凍を海水炎水化方法にある。

以下本発明の一実が施例を第4図によつて説明する。13は海水ポン:ブ12で送り込まれた海水11とLNGポンプ:14で供給されたLNG15を直接々触する晶析材構、16は気化したNG、17は晶析槽13か(ら排出されたハイドレートを

トは滅圧分解され、NNG16と水分に分かれるが、 分解熱により、水は氷水に変換する。この時分解時 間を10分以上とする。次に、梅水と氷からなる スラリーは分解槽166から分離槽18へ移送され、 分離槽18ではスラリリーは氷とプライン19に分 離される。プライン 11 9 はプラインポンプ 2 0 に より排出されるが、-一部は循環水21として循環 ポンプ22により晶も析槽13に返される。分離槽 18で分離された氷はは融解槽23で生成した炎水 24の一部24Aでも洗浄した後、融解槽23から 炎水24Bを循環ポ∶ンプ25により循環させて氷 を融解槽23に移送っする。 殿解槽23では海水 26を間接々触させナ氷を融解し、淡水24を生成 する。炎水24は炎i水ポンプ27により利用施設 へ供給される。氷の4艘解に使用された海水26は 冷梅水28になり、,晶析槽13に投入する梅水の 1部として利用されし、冷熱の有効利用度を高めて いる。

本発明は前述したこ如く、ハイドレートを成圧分 解し氷晶へと転換し、氷晶をプラインから分離し、

## 指開昭58-109179(3)

洗浄し炭水を回収するものであるが、 第3凶に示したように、急酸なる減圧分解を行なつた場合、 生成する氷晶の粒径もハイドレートの粒径と近い ものとなり、プラインからの分離性能の向上はの ぞめない。 第5凶は晶析圧力から常圧にまで減圧 する時間とその時生成した氷晶の粒径を示した。 分解時間が短かい時は、粒径が細かいが、分解時間を長くすることにより生成する氷晶粒径を大き くすることが可能である。

10分以上ではその粒径の大きさはほぼ一定に近づく。分解時間7分で飽和値の75%程度まで粒径が増大する。そのため7分以上あれば十分と考えられる。

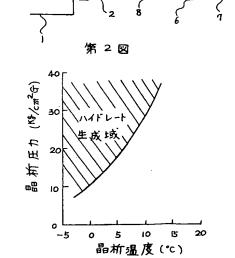
本発明によれば、LNGと海水とを直接々触して生成するハイドレートを有効に嵌水として回収することができる。

#### 図面の簡単な説明

第1 図はLNGと海水の直接々触の熱交を示す 説明図、第2 図はハイドレートの生成域を示す線 図、第3 図はハイドレートの模式図、第4 図は本 発明の一実施例を示す「プロック図、第5図は晶析 圧力から常圧まで減圧E分解と氷晶の粒径の関係を 示す線図である。

1 1 ···海水、1 5 ··· LL NG、9 ··· 高析槽、1 7 ···
分解槽、1 8 ··· 分離槽、2 3 ··· 故解槽、2 4 ··· 炎水、2 8 ··· 冷海水。





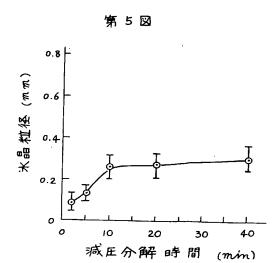
(a) ) (4)

Hallo H

14 13 25 24B 23 24B 23 17 P 18 P 16 24 26 20 27 P 28

第4[図

# 特開昭58-109179(4)



第1頁の続き ⑦発 明 者: 髙橋燦吉

日立市幸町3丁目1番1号株式 会社日立製作所日立研究所内

⑪出 願 人、 株式会社日立製作所

東京都千代田区丸の内一丁目5

番1号

[Page 435, upper half of the page]

(19) Japanese Patent Office (JP)

(12) Laid-Open Patent Gazette (A)

(11) Patent Application Laid-Open: Sho 58-109179

(51) Int. Cl.<sup>3</sup> Identification Codes Office Reference No. (43) Laid-Open Date: June 29,

Showa 58 (1983)

C 02 F 1/22

6685-4D

Number of Inventions: 1

Request for Examination: Yet to be

made

(4 pages in total)

(54) LNG direct contact frozen seawater desalination method

(21) Patent Application No.: Sho 56-206983

(22) Date of Patent Application: December 23, Showa 56 (1981)

(72) Inventor:

Takehiko Uchigami

2-39-25, Sagamigaoka, Zama City

(72) Inventor:

Nobuo Nikaido

4-20-13, Taen Chofu, Ota-ku, Tokyo

(72) Inventor:

Narioki, Nishimura

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(72) Inventor:

Tetsuro Adachi

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(72) Inventor:

Toshimi Mutsukushi[or Rokushi]

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(72) Inventor:

Katsuya Eto

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(71) Applicant:

Tokyo Gas Co., Ltd.

1-2-16, Yaesu, Chuo-ku, Tokyo

(74) Agent:

Patent Attorney [Benrishi] Akio Takahashi

To be continued onto the last page.

[Page 435, lower half of the page] [Page 435, left-hand column]

Specification

Title of the Invention: LNG direct contact frozen seawater desalination method

Claims:

- 1. In an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method characterized by allowing LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated.
- 2. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the duration of hydrate decomposition under reduced pressure being 7 minutes or longer.
- 3. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the seawater used for the ice to melt being used for the direct contact with the LNG.

# Detailed Description of the Invention:

The present invention relates to a seawater desalination method whereby LNG (liquified natural gas) and seawater are brought into direct contact.

In recent years due to the worsening petroleum situation and the direction towards clean energy the amount of LNG used has been on the rise over the years.

# [Page 435, right-hand column]

LNG is cooled and liquified in the production region and transported to the region where it is consumed. In the region where it is consumed it is heated and gasified to be used. Since LNG possesses about 200 Kcal/kg as cold heat, what is regarded important from the standpoint of energy-saving [the Chinese character in the Japanese text the translator translated as Asaving@ here is not a character ordinarily used in a phrase Aenergy-saving@ but a Chinese character for Aerase, eliminate, etc.,@ with the same vocalization. Thus the translator believes the Chinese character intended here was that for Asave@ and not Aerase@ judged from the context.] is to work out an effective utilization thereof.

While (1) open rack method and (2) submerge method have conventionally been employed as a method of gasifying LNG, neither method can effectively utilize cold heat LNG possesses. As a method of utilizing LNG=s cold heat, cold heat power generation, low-temperature storage, seawater desalination, etc., can be considered. Methods of desalinating seawater are a method whereby LNG=s cold heat is transferred to a refrigerant with a high boiling point and this refrigerant and seawater are placed in direct contact and a method whereby LNG and seawater are placed in direct contact. There is no heat exchanger with the method whereby LNG and seawater are placed in direct contact, the heat exchange property thereof being extremely good, being capable of transferring the cold heat of LNG to seawater and of making LNG into NG (natural gas). The flow of this direct contact method is illustrated in Fig. 1.

#### [Page 436, upper left-hand column]

1 refers to seawater, 2 to a seawater pump, 4 to LNG, and 5 to an LNG pump, and seawater 1 and LNG 4 are brought in direct contact in a crystallization tank 8, LNG 4 transferring cold heat to the seawater to become NG 3. At that time, as the volume of seawater 1 is reduced with respect to LNG 4, ice crystals and a hydrate (hydrocarbon hydrate) are formed in the seawater. The amount of hydrate formed varies depending on the composition of LNG, crystallization pressure,

and crystallization temperature. In addition, 6 refers to a brine pump, and 7 to brine. Fig. 2 indicates the formation region of LNG hydrate of CH<sub>4</sub> 89 mol%, and when the pressure is 10 Kg/cm<sup>2</sup> G or greater, the generation thereof begins to be marked. The result of the basic study has shown that the formation of hydrate takes precedence over that of ice in the region wherein hydrate is formed. And, we learned that hydrate is hardly formed when the crystallization pressure is 10 kg/cm<sup>2</sup> G or less and that the generation of ice takes precedence. Hydrate is, as illustratively shown in Figs. 3 (a) and (b), a hydrocarbon molecule surrounded with water molecules around it through hydrogen bonding, and is converted into an ice crystal as the hydrocarbon at the center is easily gasified under reduced pressure.

#### [Page 436, upper right-hand column]

While hydrate is in a crystal form, it is difficult to separate solid from liquid since the size of hydrate particles formed by the direct contact of LNG and seawater is on the order of about 40  $\Phi$ m, and there is no possibility of the method of separating and washing them in the state of hydrate becoming a reality.

The present invention was made with the above-described situation in view, and aims at effectively recovering as fresh water hydrate formed by LNG and seawater being brought into direct contact.

Namely, the characteristic of the present invention lies with, in an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method which allows LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated

In the following one example of the present invention will be described on the basis of Fig. 4. 13 refers to a crystallization tank wherein seawater 11 fed in by a seawater pump 12 and LNG 15 supplied by an LNG pump 14 are brought into direct contact, 16 to vaporized NG, 17 to the decomposition tank wherein the hydrate discharged from the crystallization tank 13 is decomposed under reduced pressure and converted into ice,

# [Page 436, lower left-hand column]

18 to a dissociation tank dissociating the slurry composed of seawater and ice into ice and brine, and 23 to a melting tank wherein ice and seawater 26 are brought into an indirect contact and melted. 19 refers to the brine dissociated in the dissociation tank 18, 20 to the brine pump therefor, 21 to the circulation water circulating a portion of brine 19 back to the crystallization tank 13, 22 to the circulation pump therefor, and 24 to the fresh water formed in the melting tank 23, a portion of which is used as washing water 24A to wash the ice in the dissociation tank 18. 25 refers to the circulation pump circulating the fresh water 24B formed in the melting tank 23 back to the dissociation tank 18, 27 to a fresh water pump, 28 to cold seawater, and 29 to a washing water pump.

Now, seawater 11 is fed into the crystallization tank 13 by the seawater pump 12 and comes into direct contact with LNG 15 supplied by LNG pump 14. LNG 15 robs heat off seawater 11 to become NG 16 and discharged from the crystallization tank 13, and a portion of the NG reacts with seawater 11 to form a hydrate. The slurry composed of seawater and hydrate is transferred from the crystallization tank 13 to the decomposition tank 17.

[Page 436, lower right-hand column]

While the hydrate decomposes in the decomposition tank 17 under reduced pressure and dissociates into NG 16 and the water content, due to decomposition heat water converts into ice. The decomposition time then is to be 10 minutes or longer. Next, the slurry composed of seawater and ice is transferred from the decomposition tank 16 to the dissociation tank 18, and in the dissociation tank 18 the slurry dissociates into ice and brine 19. While brine 19 is discharged with the brine pump 20, a portion thereof is returned to the crystallization tank 13 as circulation water 21 with the circulation pump 22. The ice dissociated in the dissociation tank 18 is, after being washed with a portion 24A of fresh water 24 formed in the melting tank 23, transferred to the melting tank 23 as the fresh water 24B is circulated from the melting tank 23 with the circulation pump 25. In melting tank 23, ice is melted by the seawater 26 being brought into indirect contact to form fresh water 24. Fresh water 24 is supplied to the utilization facility by the fresh water pump 27. Seawater 26 used to melt ice becomes cold seawater 28 and utilized as part of the seawater introduced into the crystallization tank 13 to enhance the degree of effective utilization of cold heat.

While the present invention is, as previously described, to decompose hydrate under reduced pressure to be converted into ice crystals, to dissociate ice crystals from brine and to wash [them] and recover fresh water,

[Page 437, upper left-hand column]

the particle diameter of the ice crystal formed when the decomposition is rapidly performed under reduced pressure results in being close to the particle diameter of the hydrate, as shown in Fig. 3, and an enhanced dissociation performance from brine cannot be anticipated. Fig. 5 illustrates the duration of pressure reductio from crystallization pressure to ambient pressure and the particle diameters of ice crystals formed then. While the particle diameter is small when the decomposition time is short, it is possible to increase by lengthening decomposition time the ice crystal particle diameter formed.

For [the decomposition time of] 10 minutes or longer, the size of the particle diameter thereof reaches to a nearly constant [value]. At the decomposition time 7 minutes the particle diameter increases to about 75% of the saturation value. Accordingly, it is thought that 7 minutes or longer would be sufficient.

According to the present invention, the hydrate formed by LNG and seawater being brought into direct contact can be effectively recovered as fresh water.

Brief Description of the Drawings:

Fig. 1 is an descriptive diagram illustrating the heat exchange of LNG and seawater in direct contact, Fig. 2 a line graph illustrating the region of hydrate formed, Fig. 3 graphical drawings of hydrate,

[Page 437, upper right-hand column]

Fig. 4 a block diagram illustrating an example of the present invention, and Fig. 5 a line graph illustrating the relation between the decomposition under reduced pressure from crystallization pressure to ambient pressure and the particle diameters of the ice crystals.

11.....Seawater, 15.....LNG, 9.....Crystallization tank, 17.....Decomposition tank,

18....Dissociation tank, 23....Melting tank, 24....Fresh water, 28....Cold seawater.

Agent Patent Attorney [Benrishi] Akio Takahashi (seal)

[Lower portion of the page]

Fig. 1

Fig. 3

(a)

(b) ·

[Drawing]

[Drawing]

[Drawing]

Fig. 2

Fig. 4

[Drawing]

[Graph]

[Label for Y axis]

Crystallization pressure

[Label for X axis]

Crystallization temperature

[Label for the area with oblique lines between

the axes]

Hydrate formation region

[Page 438, upper left-hand portion of the page]

[Graph]

[Label for Y axis]

Ice crystal particle diameter

[Label for X axis]

Reduced pressure decomposition time

[Page 438, upper right-hand portion of the page]

Continued from page 1.

(72) Inventor:

Akiyoshi Takahashi

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(71) Applicant:

Hitachi, Ltd.

1-5-1, Marunouchi, Chiyoda-ku, Tokyo

[Page 435, upper half of the page]

(19) Japanese Patent Office (JP)

(12) Laid-Open Patent Gazette (A)

(11) Patent Application Laid-Open: Sho 58-109179

(51) Int. Cl.<sup>3</sup> Identification Codes Office Reference No. (43) Laid-Open Date: June 29,

Showa 58 (1983)

C 02 F 1/22

6685-4D

Number of Inventions: 1

Request for Examination: Yet to be

made

(4 pages in total)

(54) LNG direct contact frozen seawater desalination method

(21) Patent Application No.: Sho 56-206983

(22) Date of Patent Application: December 23, Showa 56 (1981)

(72) Inventor:

Takehiko Uchigami

2-39-25, Sagamigaoka, Zama City

(72) Inventor:

Nobuo Nikaido

4-20-13, Taen Chofu, Ota-ku, Tokyo

(72) Inventor:

Narioki, Nishimura

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(72) Inventor:

Tetsuro Adachi

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(72) Inventor:

Toshimi Mutsukushi[or Rokushi]

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(72) Inventor:

Katsuva Eto

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(71) Applicant:

Tokyo Gas Co., Ltd.

1-2-16, Yaesu, Chuo-ku, Tokyo

(74) Agent:

Patent Attorney [Benrishi] Akio Takahashi

To be continued onto the last page.

[Page 435, lower half of the page] [Page 435, left-hand column]

Specification

Title of the Invention: LNG direct contact frozen seawater desalination method

Claims:

- 1. In an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method characterized by allowing LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated.
- 2. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the duration of hydrate decomposition under reduced pressure being 7 minutes or longer.
- 3. An LNG direct contact frozen seawater desalination method as set forth in claim 1, characterized by the seawater used for the ice to melt being used for the direct contact with the LNG.

# Detailed Description of the Invention:

The present invention relates to a seawater desalination method whereby LNG (liquified natural gas) and seawater are brought into direct contact.

In recent years due to the worsening petroleum situation and the direction towards clean energy the amount of LNG used has been on the rise over the years.

# [Page 435, right-hand column]

LNG is cooled and liquified in the production region and transported to the region where it is consumed. In the region where it is consumed it is heated and gasified to be used. Since LNG possesses about 200 Kcal/kg as cold heat, what is regarded important from the standpoint of energy-saving [the Chinese character in the Japanese text the translator translated as Asaving@ here is not a character ordinarily used in a phrase Aenergy-saving@ but a Chinese character for Aerase, eliminate, etc.,@ with the same vocalization. Thus the translator believes the Chinese character intended here was that for Asave@ and not Aerase@ judged from the context.] is to work out an effective utilization thereof.

While (1) open rack method and (2) submerge method have conventionally been employed as a method of gasifying LNG, neither method can effectively utilize cold heat LNG possesses. As a method of utilizing LNG=s cold heat, cold heat power generation, low-temperature storage, seawater desalination, etc., can be considered. Methods of desalinating seawater are a method whereby LNG=s cold heat is transferred to a refrigerant with a high boiling point and this refrigerant and seawater are placed in direct contact and a method whereby LNG and seawater are placed in direct contact. There is no heat exchanger with the method whereby LNG and seawater are placed in direct contact, the heat exchange property thereof being extremely good, being capable of transferring the cold heat of LNG to seawater and of making LNG into NG (natural gas). The flow of this direct contact method is illustrated in Fig. 1.

# [Page 436, upper left-hand column]

1 refers to seawater, 2 to a seawater pump, 4 to LNG, and 5 to an LNG pump, and seawater 1 and LNG 4 are brought in direct contact in a crystallization tank 8, LNG 4 transferring cold heat to the seawater to become NG 3. At that time, as the volume of seawater 1 is reduced with respect to LNG 4, ice crystals and a hydrate (hydrocarbon hydrate) are formed in the seawater. The amount of hydrate formed varies depending on the composition of LNG, crystallization pressure,

and crystallization temperature. In addition, 6 refers to a brine pump, and 7 to brine. Fig. 2 indicates the formation region of LNG hydrate of CH<sub>4</sub> 89 mol%, and when the pressure is 10 Kg/cm<sup>2</sup> G or greater, the generation thereof begins to be marked. The result of the basic study has shown that the formation of hydrate takes precedence over that of ice in the region wherein hydrate is formed. And, we learned that hydrate is hardly formed when the crystallization pressure is 10 kg/cm<sup>2</sup> G or less and that the generation of ice takes precedence. Hydrate is, as illustratively shown in Figs. 3 (a) and (b), a hydrocarbon molecule surrounded with water molecules around it through hydrogen bonding, and is converted into an ice crystal as the hydrocarbon at the center is easily gasified under reduced pressure.

## [Page 436, upper right-hand column]

While hydrate is in a crystal form, it is difficult to separate solid from liquid since the size of hydrate particles formed by the direct contact of LNG and seawater is on the order of about 40  $\Phi$ m, and there is no possibility of the method of separating and washing them in the state of hydrate becoming a reality.

The present invention was made with the above-described situation in view, and aims at effectively recovering as fresh water hydrate formed by LNG and seawater being brought into direct contact.

Namely, the characteristic of the present invention lies with, in an LNG vaporization method whereby LNG is gasified, an LNG direct contact frozen seawater desalination method which allows LNG and seawater to come in direct contact, the hydrate formed by this direct contact to decompose under reduced pressure such that it is converted into ice, and subsequent to that this ice to dissociate from the seawater and at the same time to melt to be desalinated

In the following one example of the present invention will be described on the basis of Fig. 4. 13 refers to a crystallization tank wherein seawater 11 fed in by a seawater pump 12 and LNG 15 supplied by an LNG pump 14 are brought into direct contact, 16 to vaporized NG, 17 to the decomposition tank wherein the hydrate discharged from the crystallization tank 13 is decomposed under reduced pressure and converted into ice,

## [Page 436, lower left-hand column]

18 to a dissociation tank dissociating the slurry composed of seawater and ice into ice and brine, and 23 to a melting tank wherein ice and seawater 26 are brought into an indirect contact and melted. 19 refers to the brine dissociated in the dissociation tank 18, 20 to the brine pump therefor, 21 to the circulation water circulating a portion of brine 19 back to the crystallization tank 13, 22 to the circulation pump therefor, and 24 to the fresh water formed in the melting tank 23, a portion of which is used as washing water 24A to wash the ice in the dissociation tank 18. 25 refers to the circulation pump circulating the fresh water 24B formed in the melting tank 23 back to the dissociation tank 18, 27 to a fresh water pump, 28 to cold seawater, and 29 to a washing water pump.

Now, seawater 11 is fed into the crystallization tank 13 by the seawater pump 12 and comes into direct contact with LNG 15 supplied by LNG pump 14. LNG 15 robs heat off seawater 11 to become NG 16 and discharged from the crystallization tank 13, and a portion of the NG reacts with seawater 11 to form a hydrate. The slurry composed of seawater and hydrate is transferred from the crystallization tank 13 to the decomposition tank 17.

#### [Page 436, lower right-hand column]

While the hydrate decomposes in the decomposition tank 17 under reduced pressure and dissociates into NG 16 and the water content, due to decomposition heat water converts into ice. The decomposition time then is to be 10 minutes or longer. Next, the slurry composed of seawater and ice is transferred from the decomposition tank 16 to the dissociation tank 18, and in the dissociation tank 18 the slurry dissociates into ice and brine 19. While brine 19 is discharged with the brine pump 20, a portion thereof is returned to the crystallization tank 13 as circulation water 21 with the circulation pump 22. The ice dissociated in the dissociation tank 18 is, after being washed with a portion 24A of fresh water 24 formed in the melting tank 23, transferred to the melting tank 23 as the fresh water 24B is circulated from the melting tank 23 with the circulation pump 25. In melting tank 23, ice is melted by the seawater 26 being brought into indirect contact to form fresh water 24. Fresh water 24 is supplied to the utilization facility by the fresh water pump 27. Seawater 26 used to melt ice becomes cold seawater 28 and utilized as part of the seawater introduced into the crystallization tank 13 to enhance the degree of effective utilization of cold heat.

While the present invention is, as previously described, to decompose hydrate under reduced pressure to be converted into ice crystals, to dissociate ice crystals from brine and to wash [them] and recover fresh water,

# [Page 437, upper left-hand column]

the particle diameter of the ice crystal formed when the decomposition is rapidly performed under reduced pressure results in being close to the particle diameter of the hydrate, as shown in Fig. 3, and an enhanced dissociation performance from brine cannot be anticipated. Fig. 5 illustrates the duration of pressure reductio from crystallization pressure to ambient pressure and the particle diameters of ice crystals formed then. While the particle diameter is small when the decomposition time is short, it is possible to increase by lengthening decomposition time the ice crystal particle diameter formed.

For [the decomposition time of] 10 minutes or longer, the size of the particle diameter thereof reaches to a nearly constant [value]. At the decomposition time 7 minutes the particle diameter increases to about 75% of the saturation value. Accordingly, it is thought that 7 minutes or longer would be sufficient.

According to the present invention, the hydrate formed by LNG and seawater being brought into direct contact can be effectively recovered as fresh water.

# Brief Description of the Drawings:

Fig. 1 is an descriptive diagram illustrating the heat exchange of LNG and seawater in direct contact, Fig. 2 a line graph illustrating the region of hydrate formed, Fig. 3 graphical drawings of hydrate,

# [Page 437, upper right-hand column]

Fig. 4 a block diagram illustrating an example of the present invention, and Fig. 5 a line graph illustrating the relation between the decomposition under reduced pressure from crystallization pressure to ambient pressure and the particle diameters of the ice crystals.

11....Seawater, 15....LNG, 9....Crystallization tank, 17....Decomposition tank,

18.....Dissociation tank, 23.....Melting tank, 24.....Fresh water, 28.....Cold seawater.

Agent Patent Attorney [Benrishi] Akio Takahashi (seal)

[Lower portion of the page]

Fig. 1

Fig. 3

(a)

(b)

[Drawing]

[Drawing]

[Drawing]

Fig. 2

Fig. 4

[Drawing]

[Graph]

[Label for Y axis]

Crystallization pressure

[Label for X axis]

Crystallization temperature

[Label for the area with oblique lines between

the axes]

Hydrate formation region

[Page 438, upper left-hand portion of the page]

[Graph]

[Label for Y axis]

Ice crystal particle diameter

[Label for X axis]

Reduced pressure decomposition time

[Page 438, upper right-hand portion of the page]

Continued from page 1.

(72) Inventor:

Akiyoshi Takahashi

c/o Hitachi Research Laboratory, Hitachi, Ltd.,

3-1-1, Saki-machi, Hitachi City

(71) Applicant:

Hitachi, Ltd.

1-5-1, Marunouchi, Chiyoda-ku, Tokyo